



Short communication

Enhanced storage property of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ coated with LiCoO_2 Wanmin Liu^{a,b,*}, Guorong Hu^b, Ke Du^b, Zhongdong Peng^b, Yanbing Cao^b^a School of Chemistry and Chemical Engineering, Hunan Institute of Engineering, Xiangtan 411104, China^b School of Metallurgical Science and Engineering, Central South University, 932 Lushan South Road, Changsha 410083, China

HIGHLIGHTS

- ▶ LiCoO_2 -coated $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ shows better storage stability compared to $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$.
- ▶ The properties of LiCoO_2 -coated $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ have almost nothing to do with the air humidity.
- ▶ LiCoO_2 -coated $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ is resistant to H_2O and CO_2 in air.
- ▶ The LiCoO_2 coating layer suppresses effectively the reactions between $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ and atmosphere.

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ABSTRACT

The storage properties of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ and LiCoO_2 -coated $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ have been investigated comparatively. It is found that the latter exhibits better storage stability than the former. After storage in air at different relative humidities, LiCoO_2 -coated $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ shows little changes in the aspects of weight, nickel oxidation state, moisture and carbon contents and electrochemical performance. However, for $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$, the higher the air humidity is, the bigger these aspects change. Fourier transformed infrared (FTIR) spectrum reveals that LiCoO_2 -coated $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ is resistant to H_2O and CO_2 in air. X-ray photoelectron spectroscopy gives evidence that the LiCoO_2 coating layer suppresses effectively the reactions between $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ and atmosphere, which contributes to the enhancement of storage performance of LiCoO_2 -coated $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$.

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1. Introduction

In recent years, nickel-rich LiNiO_2 -based cathode materials $\text{LiNi}_{1-x-y}\text{Co}_x\text{M}_y\text{O}_2$ ($0.8 \leq 1-x-y \leq 1$, $\text{M} = \text{Al}$, Mn and Mg , et al.) have been intensively investigated for replacing currently used LiCoO_2 in lithium-ion batteries [1–10]. Most studies are focused mainly on synthesis methods [11–18] and surface coating [19–26] in order to optimize their electrochemical performance and thermal stability. However, the chemical stability during storage is also an important property for practical cathode materials.

It has been recognized that $\text{CO}_2/\text{H}_2\text{O}$ in air and the spontaneous reduction of Ni^{3+} to Ni^{2+} on the surface of $\text{LiNi}_{1-x-y}\text{Co}_x\text{M}_y\text{O}_2$ materials are the two major causes of the formation of $\text{Li}_2\text{CO}_3/\text{LiOH}$, and the presence of surface $\text{Li}_2\text{CO}_3/\text{LiOH}$ is the main source of poor

storage property of $\text{LiNi}_{1-x-y}\text{Co}_x\text{M}_y\text{O}_2$ [27–33]. Besides, $\text{Li}_2\text{CO}_3/\text{LiOH}$ on the surface can result in safety issues [34,35].

Based on the formation reason of $\text{Li}_2\text{CO}_3/\text{LiOH}$, some approaches improved the storage performance of $\text{LiNi}_{1-x-y}\text{Co}_x\text{M}_y\text{O}_2$ have been exploited and are summarized as follows. (i) Reduce nickel content or increase cobalt content in the compound. Liu et al. reported that the storage property of $\text{LiNi}_{0.75}\text{Co}_{0.2}\text{Ti}_{0.05}\text{O}_2$ was superior to that of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$, the discharge specific capacity of the former only lost 11% after storage in air for 6 months, while the latter had a capacity loss of 21% for the same conditions [36]. Eom et al. reported that the storage performance of $\text{LiNi}_{0.8}\text{Co}_{0.16}\text{Mn}_{0.04}\text{O}_2$ was better than that of $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$, with exposure to air with a relative humidity of 40% for 7 days, the former showed 1700 and 1650 ppm for moisture (OH in LiOH) and carbon (C in Li_2CO_3), respectively, while the latter showed 4540 and 3590 ppm for moisture and carbon, respectively [33]. Li et al. even reported that the storage stability of $\text{LiNi}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}\text{O}_2$ was very good, and the surface reaction between $\text{LiNi}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}\text{O}_2$ and $\text{CO}_2/\text{H}_2\text{O}$ was so negligible that it could not affect distinctively the electrochemical performance of the materials [37]. (ii) Store the material in an inert atmosphere

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without CO_2 and H_2O . Liu et al. showed the discharge specific capacities of the fresh and stored $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ materials. The fresh $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ sample had the discharge capacity of 180 mAh g^{-1} , the sample stored in Ar for 6 months delivered 168 mAh g^{-1} , while the sample stored in air for 6 months only showed 142 mAh g^{-1} [36]. (iii) Mix physically LiNiO_2 -based cathode materials with other cathode materials. The storage performance of $\text{LiCoO}_2/\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ was investigated by Mijung et al., and they found that the cathode with a LiCoO_2 to $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ weight ratio of 4:1 showed significantly lower LiOH and Li_2CO_3 levels upon air exposure compared with the individual $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ [38]. (iv) Wash the material in water. Kim et al. investigated the washing effect of a $\text{LiNi}_{0.83}\text{Co}_{0.15}\text{Al}_{0.02}\text{O}_2$ cathode in water. They found that the formation of LiOH and Li_2CO_3 impurities on $\text{LiNi}_{0.83}\text{Co}_{0.15}\text{Al}_{0.02}\text{O}_2$ powders could be reduced without structural degradation by washing in water. Although the as-synthesized sample had a moisture content of 570 ppm immediately after firing, this level increased rapidly to 1270 ppm in air with a relative humidity of 50%. However, its content was decreased to 210 ppm after washing twice in water, followed by heat-treatment at 700°C [35]. (v) Coat the material with an electrochemically active layer. Kim et al. reported that the $\text{Co}_3(\text{PO}_4)_2$ coating material could react with LiOH and Li_2CO_3 impurities dissolved from the bulk $\text{LiNi}_{0.8}\text{Co}_{0.16}\text{Al}_{0.04}\text{O}_2$ material and the storage property of the coated cathode was improved remarkably [39]. Through analyzing the above approaches, the fifth method is the most reasonable in view of the aim of high capacity of nickel-rich LiNiO_2 -based cathode materials. Moreover, the coated or gradient cathode materials, which are based on the nickel-rich LiNiO_2 -based cathode materials as the bulk phase and other electrochemical active materials as the exterior phase, have attracted extensive research interest [40–44].

Recently, our group reported that an electrochemically active LiCoO_2 layer was coated on the surface of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ and the coating thickness was about 50 nm [45]. However, this study reported electrochemical properties only. In this paper, we extended our investigation and examined the effect of the LiCoO_2 coating layer on the storage performance of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$.

2. Experimental

$\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ and 3 wt.% LiCoO_2 -coated $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ were synthesized by a co-oxidation-controlled crystallization method and a molten salt method, respectively, as reported in our previous work [18,45]. The storage process was carried out at room temperature by storing the as-synthesized uncoated and coated samples in air with different relative humidities for 3 months.

In order to observe the weight increase of the sample during the course of storage, the sample was weighed using an electronic balance with 0.1 mg accuracy every day until the weight didn't change obviously, then it was weighed every week. Here, the weight increasing rate (Δm) is defined as

$$\Delta m_n = \frac{m_n - m_0}{m_0} \times 100\% \quad (1)$$

where m is weight (mg), m_0 is the initial weight of the sample (mg), n ($n = 1, 2, 3, \dots$) is measuring times.

The moisture content (OH^-) in the sample was determined using a Karl-Fischer moisture titrator at 250°C (prior to measuring, the sample was vacuum dried at 150°C for 2 h to remove the H_2O molecules adsorbed on the sample). Therefore, the measured moisture was from OH^- in LiOH . The carbon content in Li_2CO_3 was measured using a CHS element analyzer at 1000°C in an oxygen atmosphere. Fourier transformed infrared (FTIR) spectrum of the

sample was obtained on Shimadzu-FTIR-8400 spectrometer. XPS analysis was performed using a Physical Electronics Quantum 2000 ESCA spectrometer.

The nickel and cobalt contents of the sample were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Optima 4300DV). The average nickel oxidation state of the sample was determined by combining iodometry with EDTA titration in Ar atmosphere [46] (the oxidation state of cobalt was regarded as +3 because of its easiness to be oxidized). And the average nickel oxidation state (OS) was calculated from the following formula:

$$\text{OS} = \frac{2 \times n(\text{Ni}^{2+}) + 3 \times n(\text{Ni}^{3+})}{n(\text{Ni})} \quad (2)$$

where n corresponds to the nickel mole number (Ni^{2+} , Ni^{3+} or total Ni) of the sample.

The electrochemical characteristics were tested using a coin-type CR2032 cell with lithium foil as the negative electrode. A positive electrode consisted of 80% active material, 10% acetylene black and 10% PVDF binder (weight ratio) on an aluminum foil. Coin-type cells were assembled in an argon filled glove box with an electrolyte of 1 mol L^{-1} LiPF_6 in EC–DMC–EMC (1:1:1, volume ratio) solution and a Celgard 2400 separator. The charge–discharge measurement was performed at a current density of 0.2 C within the voltage range of 2.8–4.3 V (vs. Li/Li^+) at room temperature on a LAND CT2001A test system.

3. Results and discussion

3.1. Change of weight

Fig. 1 shows the weight increasing rate curves of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ and LiCoO_2 -coated $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ during storage in air at relative humidities of 40%, 60% and 80%. Clearly, the weight of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powders is affected greatly by the air humidity. The bigger the relative humidity is, the more the weight of the sample increases. After 3 months, the weight of the sample stored at 40% relative humidity increases by 0.197%, while the weight of the sample stored at 80% relative humidity increases by 1.433%. Besides, the former needs 7 days to stabilize the weight, but

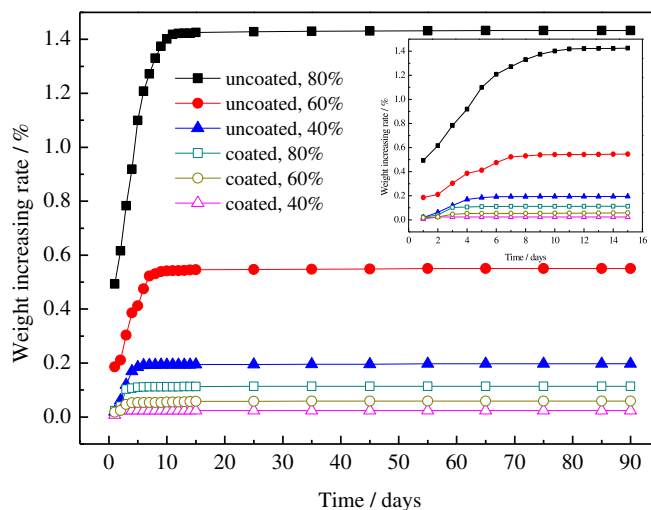


Fig. 1. Weight increasing rate curves of uncoated and LiCoO_2 -coated $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ samples during storage in air humidities of 40%, 60% and 80%. Inset shows the curves in the first 15 days.

the latter needs twofold time. Contrastively, the weight of LiCoO_2 -coated $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powders has almost nothing to do with the air humidity, and it takes the samples 3 days to stabilize the weight only. These results indicate that the storage property of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ is poor and can be improved by decreasing air humidity, while LiCoO_2 -coated $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ has excellent storage performance.

3.2. Changes of nickel oxidation state, moisture and carbon contents

Table 1 shows the nickel oxidation state, moisture and carbon contents in $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ and LiCoO_2 -coated $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powders before and after storage in air at different relative humidities. The nickel oxidation state of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ decreases from 3 of the fresh sample to 2.991, 2.953 and 2.916 of the stored samples at relative humidities of 40, 60 and 80%, respectively. The moisture content in $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ increases rapidly from 611 ppm of the fresh sample to 1758, 2623 and 3826 ppm of the stored samples at relatively humidities of 40, 60 and 80%. And the trend of the carbon content in the Li_2CO_3 of these samples is similar to that for the moisture. These results indicate that during the course of storage, a certain amount of LiOH , Li_2CO_3 and NiO is formed on the surface of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ owing to the absorption–formation of H_2CO_3 and the spontaneous reduction of Ni^{3+} to Ni^{2+} [28,35,36], and the amounts of LiOH , Li_2CO_3 and NiO are expected to increase with increasing air humidity. However, as for LiCoO_2 -coated $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$, the nickel oxidation state, moisture and carbon contents undergo little changes, irrespective of the relative humidity during storage. This may be attributed to the existence of the LiCoO_2 coating layer on the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$. On one hand, the LiCoO_2 coating layer prevents $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ from contacting directly air and depresses the reduction of Ni^{3+} . On the other hand, LiCoO_2 has good chemical stability and can resist effectively the attack of H_2CO_3 [35,38].

3.3. Electrochemical performance

Fig. 2(a) and (b) present the initial charge–discharge curves of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ and LiCoO_2 -coated $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ before and after storage in air for 3 months at different relative humidities, respectively. As shown in Fig. 2(a), freshly synthesized $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ sample has a charge specific capacity of 226.7 mAh g^{-1} and a discharge specific capacity of 196.8 mAh g^{-1} . However, the performance of the sample decreases dramatically after storage in air for 3 months. Moreover, the higher the humidity is, the more severely the property deteriorates. For instance, in the case of the sample stored at a relative humidity of 40%, the charge and discharge specific capacities drop from 226.7 to 197 mAh g^{-1}

Table 1
Nickel oxidation state (OS), moisture and carbon contents in $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ and LiCoO_2 -coated $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ before and after storage in air at different relative humidities for 3 months.

Relative humidity	$\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$			LiCoO_2 -coated $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$		
	OS	Moisture (ppm)	Carbon (ppm)	OS	Moisture (ppm)	Carbon (ppm)
Fresh	3.000	611	540	3.000	106	
40%	2.991	1758	2015	3.000	213	348
60%	2.953	2623	3057	2.999	227	356
80%	2.916	3826	4142	2.998	238	369

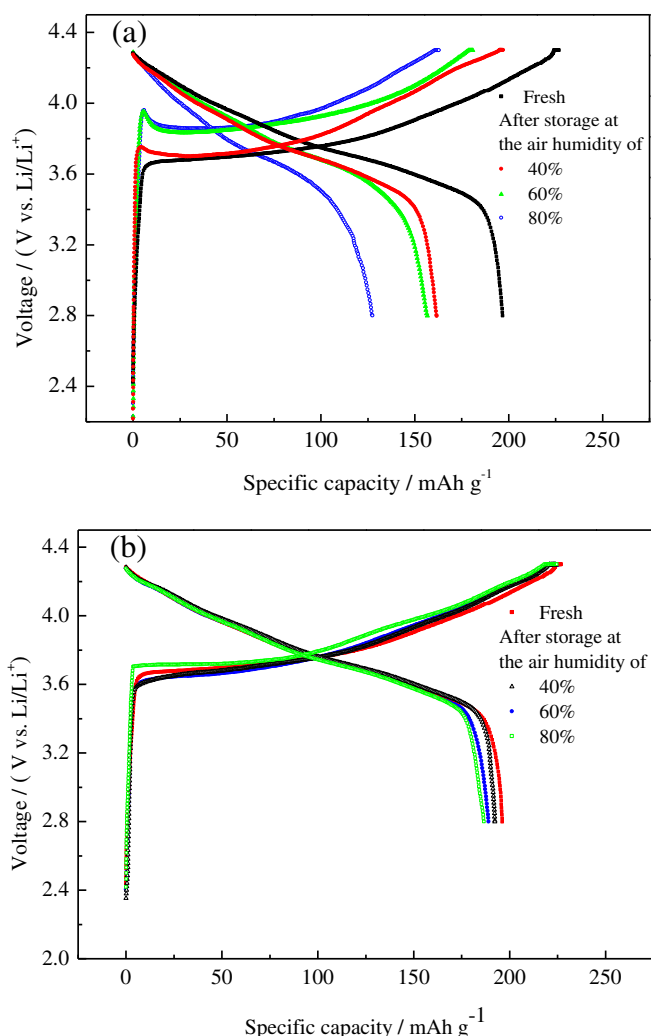


Fig. 2. Initial charge–discharge curves of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (a) and LiCoO_2 -coated $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (b) before and after storage in air at different relative humidities.

and from 196.8 to 161.7 mAh g^{-1} , respectively. In the mean time, the charge curve is $\sim 100 \text{ mV}$ higher than that of the fresh sample and the discharge curve is $\sim 100 \text{ mV}$ lower than that of the fresh sample, which indicates a larger electrochemical polarization. Especially, the sample stored at a relative humidity of 80% has only the charge and discharge specific capacities of 162.8 and 127.5 mAh g^{-1} , respectively. And the electrochemical polarization is larger than that of the sample stored at a relative humidity of 40%. On the other hand, it can be seen from Fig. 2(b) that there is little performance difference between the fresh and the stored LiCoO_2 -coated $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$. Except the sample stored at a relative humidity of 80% shows lower discharge capacity of 186.6 mAh g^{-1} than 196.2 mAh g^{-1} of the fresh material and slightly larger polarization than that of the fresh material, other stored samples almost display the same charge–discharge property as the fresh powders.

Fig. 3 compares the cycle performance of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ and LiCoO_2 -coated $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ before and after storage in air for 3 months at different relative humidities, respectively. As shown in Fig. 3(a), the cycle performance of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ is affected remarkably by the storage humidity. The discharge specific capacity of the fresh $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ only decreases from 196.8 to 189.1 mAh g^{-1} in the first 50 cycles with the capacity retention of 96.1%. However, for the samples stored at relative

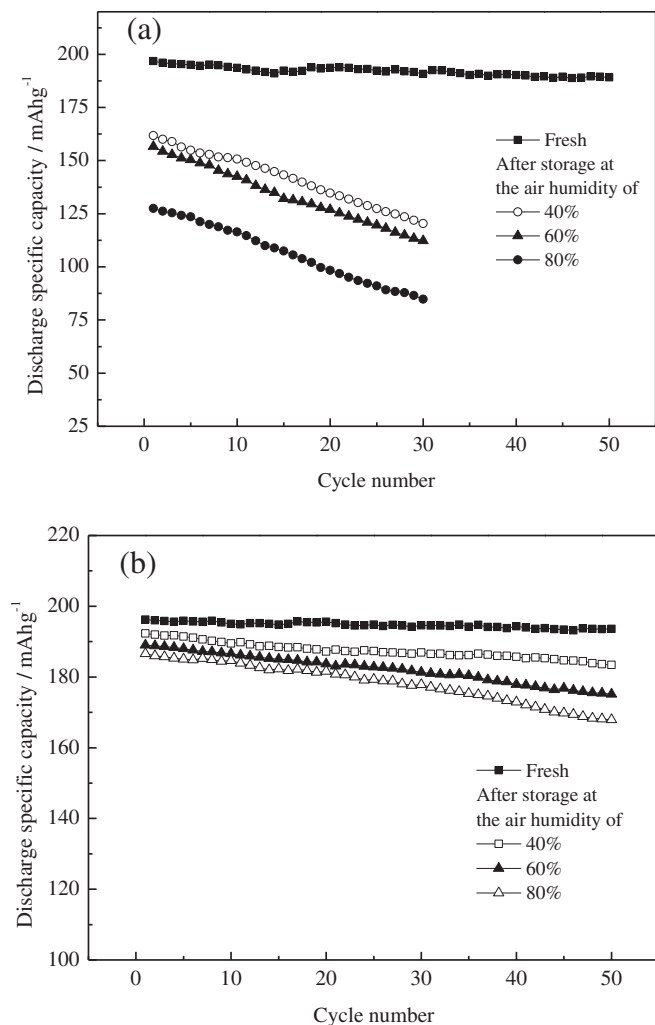


Fig. 3. Cycle performance of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (a) and LiCoO_2 -coated $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (b) before and after storage in air at different relative humidities.

humidities of 40%, 60% and 80%, the capacity retentions are about 74.46%, 71.71% and 66.51% after 30 cycles, respectively. Contrastively, it is easily found from Fig. 3(b) that LiCoO_2 -coated $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ has better cycle performance, regardless of the fresh or stored samples. For the fresh sample, the fiftieth discharge specific capacity of the coated sample is 193.6 mAh g^{-1} , with the capacity retention of 98.7% after 50 cycles. After storage at the air humidities of 40%, 60% and 80%, the samples still have the fiftieth discharge specific capacities of 183.4, 175.1 and 167.9 mAh g^{-1} , with the capacity retentions of 95.4%, 92.6% and 90%, respectively.

Therefore, from the said results, it can be concluded that the LiCoO_2 coating layer enhances markedly the storage property of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ or its electrochemical performance after storage.

3.4. FTIR studies

Fig. 4 shows FTIR spectra of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ and LiCoO_2 -coated $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ before and after storage in air at a relative humidity of 80%. As for freshly prepared $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ sample, there is one strong peak at 645 cm^{-1} , which is assigned to the MO_6 ($\text{M} = \text{Ni}, \text{Co}$) vibration [47], and one weak band $3600\text{--}3000 \text{ cm}^{-1}$, which is assigned to the O–H stretching vibration from LiOH , respectively. After storage, besides retaining

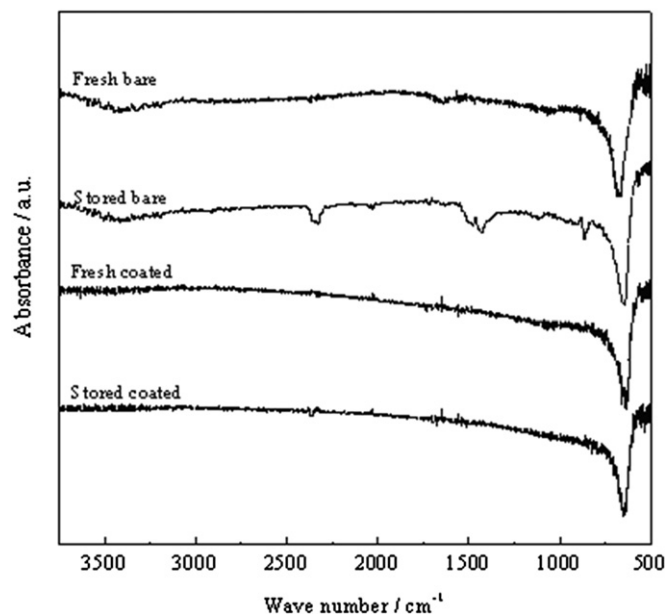


Fig. 4. FTIR spectra of bare and LiCoO_2 -coated $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ before and after storage in air at a relative humidity of 80%.

the characteristic peaks at 645 cm^{-1} and $3600\text{--}3000 \text{ cm}^{-1}$, there appears two new obvious peaks at 868 cm^{-1} and 1430 cm^{-1} which are assigned to the CO_3^{2-} vibration from Li_2CO_3 , suggesting again that there is a certain amount of Li_2CO_3 formed on the stored $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$. On the other hand, the fresh and stored LiCoO_2 -coated $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ samples have very similar FTIR spectra. They don't contain any Li_2CO_3 and LiOH peaks, suggesting a negligible amount of these phases. This indicates again that LiCoO_2 -coated $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ is resistant to H_2O and CO_2 in air.

3.5. XPS studies

To investigate further why the LiCoO_2 -coated $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ material has better storage stability than the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ material, the surface composition changes of the bare and coated samples after storage in air at a relative humidity of 80% were detected by XPS, as shown in Fig. 5. For the bare sample, Ni 2p, Co 2p and O 1s spectra before and after storage show similar changes with Liu's report. And two kinds of electrochemically inactive layers, including NiO-like species and adsorbed hydroxyl and carbonate species, are believed to be responsible for the storage loss [36]. However, for the stored LiCoO_2 -coated $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$, Ni 2p spectrum can't be measured due to the existence of 50 nm LiCoO_2 layer, while O 1s and Co 2p spectra are almost the same as that of the fresh $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$. In the O 1s spectra, the dominating peak at 528.8 eV can be assigned to the lattice oxygen, another small peak at 531.0 eV the adsorbed hydroxyl and carbonate species. As for Co 2p spectra, no obvious changes are found, and cobalt ions are always kept in trivalence before and after storage, regardless of the uncoated or coated samples. These results indicate that Co^{3+} in the layered metal oxide frame exists stably in air, and the LiCoO_2 coating layer suppresses effectively the reactions between $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ and atmosphere. Correspondingly, the amounts of the electrochemically inactive surface species on the coated material after storage are decreased greatly, which contributes to the improvement of storage property of LiCoO_2 -coated $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$.

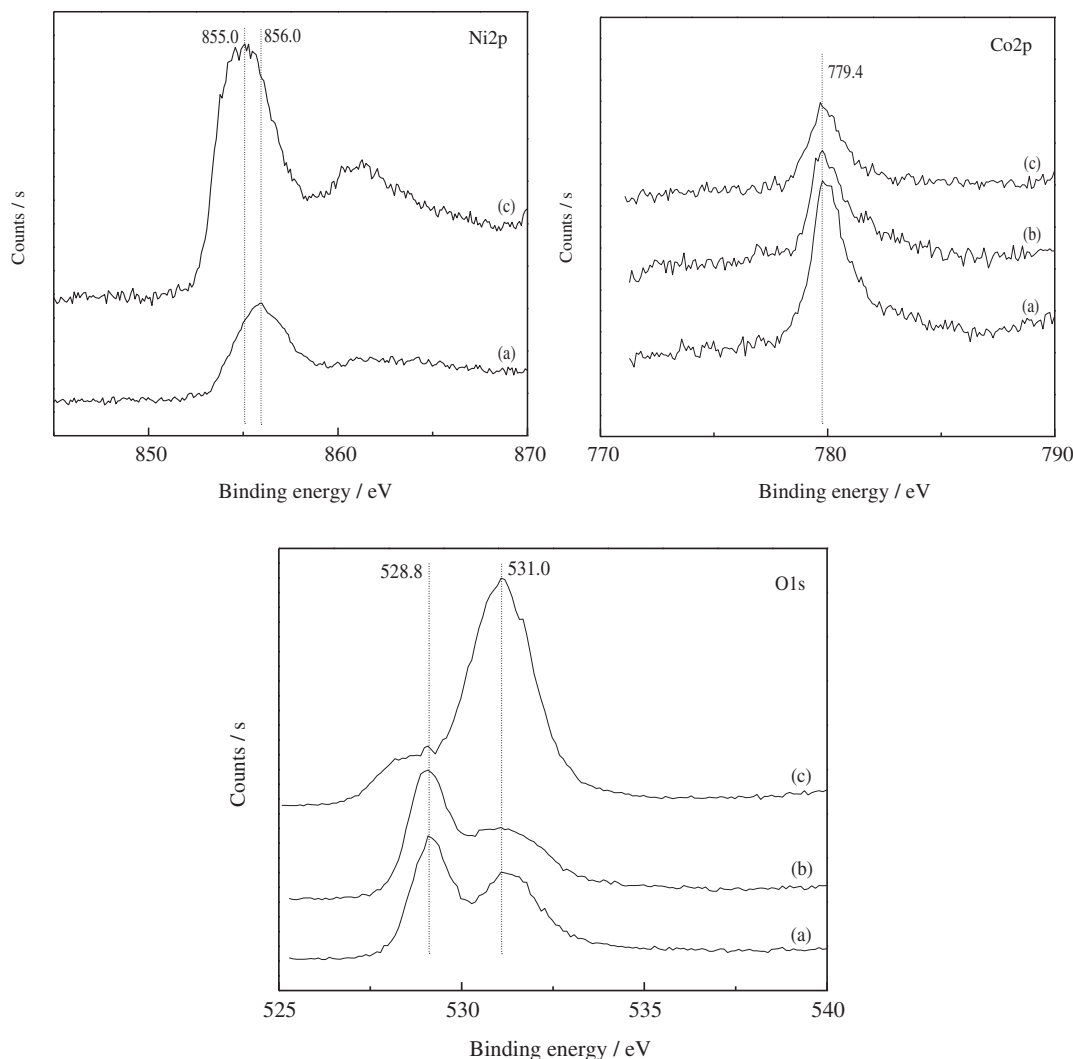


Fig. 5. Ni 2p, Co 2p and O 1s XPS spectra of bare and LiCoO_2 -coated $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$: (a) fresh bare sample; (b) stored coated sample; (c) stored bare sample.

4. Conclusions

After $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ and LiCoO_2 -coated $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ were stored at the same conditions, the latter showed less changes than the former in the aspects of weight, nickel oxidation state, moisture and carbon contents and electrochemical performance. This is due to the LiCoO_2 coating layer suppresses effectively the reactions between $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ and atmosphere, and LiCoO_2 has good chemical stability. Our experimental data indicate that storing $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ in air with lower relative humidity can improve the storage property of the material within a narrow range. The more effective approach is to coat the material with an electrochemically active layer which is resistant to H_2O and CO_2 in air.

Acknowledgments

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